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Determination of the HCl Dissociation Constant at a Temperature of 350°C and 200 Bars of Pressure by the Potentiometric Method Using a Ceramic Electrode

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Abstract—A technique has been developed for pH measurement in flow-through cells at temperatures from 175 to 350°C and pressures up to 350 bars in a nonisothermal cell consisting of a $ZrO_2(Y_2O_3)$ ceramic electrode and a Ag/AgCl (2 M KCl, 25°C) flow-through reference electrode. This technique has been applied to determination of the HCl dissociation constant at 350°C and 200 bars; previously, the HCl dissociation has not been studied sufficiently reliably under these conditions. The obtained value $pK_{dis} = 2.16 \pm 0.03$ was used to estimate the acidity of fluids from their chemical composition at the vent of high-temperature submarine hydrothermal solutions.

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INTRODUCTION

In addition to temperature and pressure, the pH value of hydrothermal fluid is an important factor that controls migration and deposition of ore components during ore formation. Therefore, direct pH measurements are necessitated, including both in natural waters at occurrences of present-day hydrothermal activity and in hydrothermal experiments.

In the last century, pH measurements at <100°C were widely applied in various fields of science and industrial activity. At present, high-temperature measurements of pH are successfully performed in experimental geochemistry using a glass electrode up to 175°C (Kryukov et al., 1966) and a hydrogen electrode up to 320°C (Mesmer et al., 1988, 1995; Macdonald et al., 1992). Moreover, using a pH-sensitive electrode made of a ZrO_2 ceramic and stabilized with Y_2O_3, it has become feasible to raise the temperature of measurements to 400–450°C. The state of the art of measurement techniques with yttria-stabilized zirconia sensors was reviewed by Lvov et al. (2003). However, precise potentiometric measurements at temperatures over 300°C have not yet become a routine procedure.

The purpose of this work is to adjust the method of high-temperature pH measurements using the ceramic electrode and to determine the HCl dissociation constant (K_{dis}) at 350°C. The point is that K_{dis} values obtained with different methods (mainly by the conductometric and solubility techniques) are widely scattered, especially near the critical point of low-density solutions (Tagirov et al., 1997; Pokrovskii, 1999). In this regard, the application of the new method of direct pH determination looks very promising.

The flow-through high-temperature potentiometric cell was designed and made at the Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Russian Academy of Sciences (Moscow, Russia). All measurements were performed at McGill University (Montreal, Canada) under the supervision of Professor A.E. Williams-Jones.

EXPERIMENTAL

Ceramic Electrode Operation

The operation mechanism and thermodynamics of a $ZrO_2(Y_2O_3)$ sensor with a Hg/HgO internal half-element were first studied by Tsuruta and Macdonald (1982) and Macdonald et al. (1988) and afterwards thoroughly reviewed by Lvov et al. (2003). The potential-forming equilibrium may be described in terms of oxygen vacancies on the solution side and on the internal contact side, respectively:

$$V_{\ddot{o}} + H_2O = O_o + 2H^+,$$

$$HgO + V_{\ddot{o}} + 2\bar{e} = Hg + O_o,$$

where $V_{\ddot{o}}$ are oxygen vacancies and O_o is the oxygen atom. Assuming that the activity of oxygen vacancies is constant throughout the ceramic and measurements are performed potentiometrically, i.e., at a zero current through the membrane, the sensor potential may be determined by the equilibrium (Lvov et al., 2003)

$$HgO + 2H^+ + 2\bar{e} = Hg + H_2O.$$

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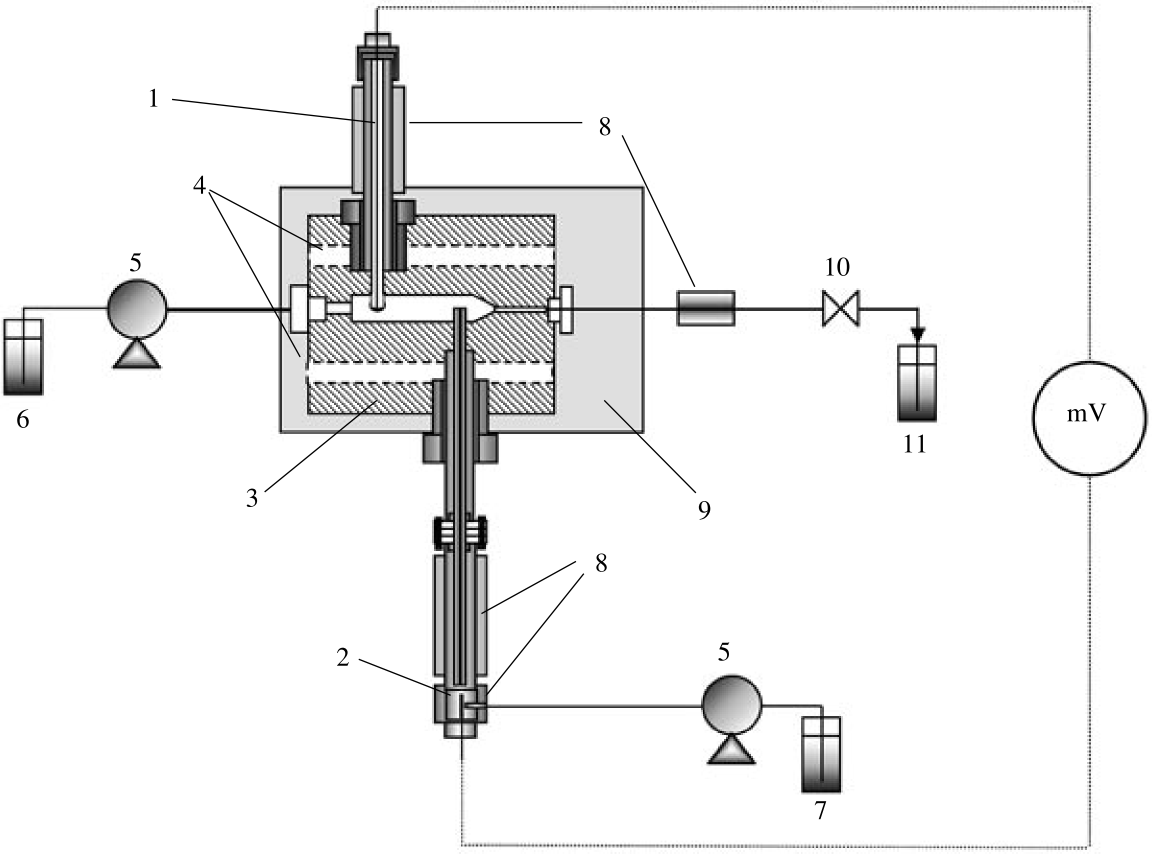

Fig. 1. Scheme of a flow-through system assigned for high-temperature potentiometric pH measurements. (1) $ZrO_2(Y_2O_3)$ ceramic pH electrode; (2) Ag/AgCl reference electrode; (3) cell body made of Ti alloy VT8; (4) heaters; (5) pumps; (6) analyzed solution; (7) 2 M KCl solution; (8) cooling; (9) thermoinsulation; (10) pressure control; (11) waste.

The Nernst equation for this equilibrium takes the form

$$E = E^0_{\mathrm{Hg/HgO}} - (2.303RT/2F)^*\log a_{\mathrm{H_2O}} - (2.303RT/F)^*\mathrm{pH},$$

where $E^0_{\mathrm{Hg/HgO}}$ is the standard potential of the Hg/HgO couple, R is the universal gas constant (8.3144 J/mol K), F is the Faraday constant (96485 C/mol), T is the temperature (K), and $a_{\mathrm{H_2O}}$ is the water activity on the solution side.

The nonisothermal cell used in this work consisted of a pH-sensitive $ZrO_2(Y_2O_3)$ ceramic electrode and a flow-through Ag/AgCl reference electrode at 25°C; they were connected by an electrolytic junction (2 M KCl) with forced efflux of the internal solution:

$$\overset{25^\circ\mathrm{C}}{\longleftrightarrow}\overset{T = 175\text{–}350^\circ\mathrm{C}}{\longleftrightarrow}\overset{25^\circ\mathrm{C}}{\longleftrightarrow}$$

$$\mathrm{Cu}|\mathrm{Ag}|\mathrm{AgCl}|2.0m\mathrm{KCl}||\text{ analyzed solution }|\mathrm{ZrO_2(Y_2O_3)}|\mathrm{HgO}|\mathrm{Hg}|\text{Fe–Ni steel}|\mathrm{Cu}.$$

Potentiometric Cell

The measurement cell is schematically shown in Fig. 1. The body of the cell and the electrode cases used in this work are made of the Ti-based alloy VT8. The $ZrO_2(Y_2O_3)$ ceramic test tube and the Al_2O_3 ceramic tube of the electrolytic junction were sealed with Graflex cones in a hot zone so as to minimize "dead" volumes. The upper parts of the electrodes were cooled by external water-cooling system.

To avoid overheating by convective flows, the reference electrode is directed downward, while the pH electrode is directed vertically upward because Hg/HgO paste was used as its internal contact. The distance between the electrodes was reduced to a minimum to avoid external electric induction.

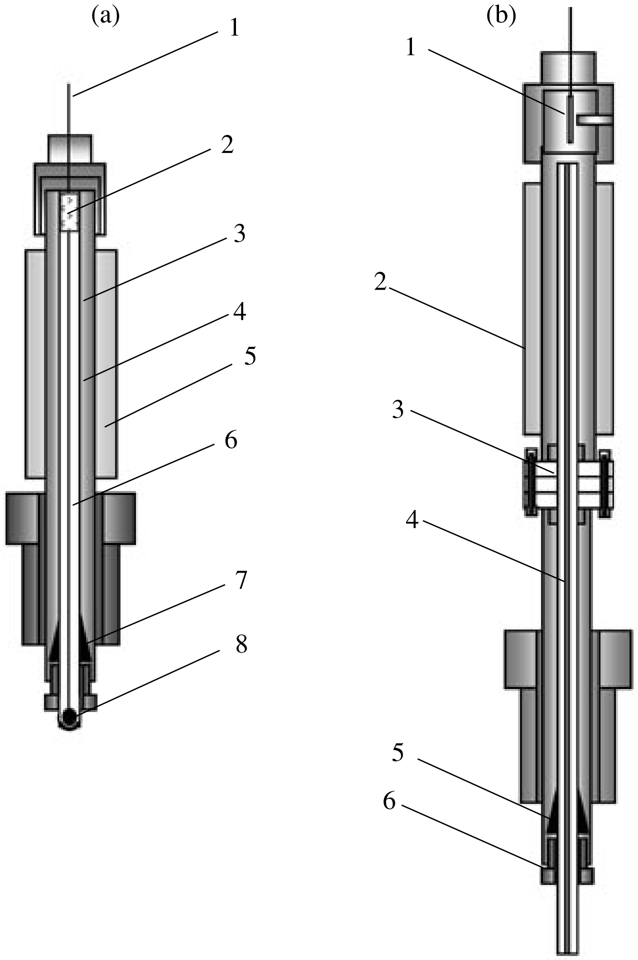

Fig. 2. Design of the (a) $ZrO_2(Y_2O_3)$ ceramic pH electrode and (b) flow-through Ag/AgCl (2 M KCl) reference electrode. (a) (1) Steel wire, (2) epoxy, (3) titanium case of electrode, (4) $ZrO_2(Y_2O_3)$ ceramic tube, (5) cooling circuit, (6) ZrO_2 powder, (7) Graflex sealing cone, and (8) Hg/HgO; (b) (1) Ag/AgCl electrode, (2) thermostating, (3) Teflon ring, (4) Al_2O_3 ceramic tube, (5) Graflex cone, and (6) hold-down nut.

$ZrO_2(Y_2O_3)$ Ceramic Electrode

A scheme of the ceramic electrode is given in Fig. 2a. The ceramic tube of the pH sensor was obtained from Degussa-Hulls (France); the outer diameter is 10 mm, and the walls are 1 mm thick. The pH sensor was made after Macdonald's technique (Hettiarachchi and Macdonald, 1984). A small amount of Hg/HgO paste was put on the bottom of a ceramic test tube, the steel wire was covered with Zr oxide powder, and the upper part of the test tube was filled in with epoxy.

Reference Electrode

An Ag/AgCl half-element produced by the thermal method and thermostated at 25°C was used as a reference electrode (Fig. 2b). The 2 M KCl solution was continuously pumped up, with an average rate of 0.1 ml/min, to eliminate the diffusion potential. The flow rate of the analyzed solution was approximately ten times higher to prevent its contamination with the reference solution (2 M KCl). For the same purpose, the outlet of the ceramic tube of the reference electrode was located last in the cell along the path of the analyzed solution. The upper part of the electrode, containing the Ag half-element, is electrically disconnected from the body of the cell by a Teflon ring.

Reagents and Experimental Techniques

All reagents used in the work had a quality grade not lower than analytical grade. The solutions were prepared on the basis of deionized MilliQ water (the resistivity was no less than 18 MΩ).

The solutions for analysis and reference were supplied to the system separately with two high-pressure pumps (Fig. 1), which could provide a flow rate from 10^{-1} to 10 ml/min and up to 350 bars of pressure. Heating was carried out and the temperature maintained by Chromalox heaters, placed into the cell body, and by an Omega CN9000A controlling device. The temperature was measured with K-type chromel–alumel thermocouples. The accuracy of temperature measurements was within ±0.5°C. The temperature of the reference electrode was maintained within 25 ± 0.1°C by a NesLab RTE5B water thermostat.

The solution pH was measured at the cell outlet at room temperature. Such control did not show any appreciable change in the composition of the solution during the experiment.

The potential drop between the ceramic sensor and the reference electrode was measured with a Fisher Scientific Accumet 25 pH meter. Pressure was controlled by a pressure sensor in a Waters 590 pump set.

The measurements were performed under a constant pressure of 200 bars and at temperatures of 175, 250, 300, and 350°C. When the solution was changed, a new solution was pumped into the system until a stable (±1 mV) potential was reached. While passing to the next temperature, the time of electrode potential settling was 2–5 min on average.

MEASUREMENT RESULTS

Calibration

The electrode system was calibrated in the acid pH range by HCl solutions with concentrations of 10^{-1}–10^{-4} mol/kg H_2O at 175, 250, and 300°C and 200 bars (Table 1). At a lower temperature, the readings were unstable because of a high resistivity of the ceramic. The calibration results are given in Fig. 3. The pH values of analyzed solutions were calculated by the GIBBS program of the HCh software package (Shvarov and Bastrakov, 1999) using the SLOP98 thermodynamic database, an updated version of the SUPCRT92 program package (Johnson et al., 1992). At all temperatures, the slope of calibrated straight lines in the E–pH coordinates (Table 2) was close to the theoretical Nernst values ($2.303RT/n$). It should be noted that the calculated pH values are virtually independent of the chosen K_{dis} HCl value at the given temperature and concentration because the content of nondissociated $HCl^0_{(aq)}$ is negligible. Deviations of particular points from approximating straight lines do not exceed ±2 mV, which corresponds to an uncertainty of ±0.015 pH unit. The closeness of the slopes of calibrated straight lines to their theoretical values implies that the values of the diffusion potential at the HCl $(10^{-1}–10^{-4})m$–KCl (2 M KCl) boundary and the thermodiffusion potential in the reference electrode are either low or do not change appreciably within the chosen range of temperatures and HCl concentrations. In any case, the calibrated system is fit for direct potentiometric pH measurements.

Dissociation Constant of HCl at 350°C and 200 Bars

It is well known that, if the temperature rises to 350°C, the HCl dissociation constant notably decreases, and the association degree strongly depends on the acid concentration. Calculation indicates that, under these conditions (350°C and 200 bars), the pH value of a very diluted HCl solution ($0.0001m$) virtually does not depend on the K_{dis} accepted in the calculation, as supported by evidence from different sources. In more concentrated solutions, the chosen K_{dis} value markedly affects the calculated pH value. These relationships may be used to determine the HCl dissociation constant.

In calculating the constant, we assume that (1) the slope in the E–pH coordinates at 350°C, as in the temperature range 175–300°C, remains theoretical and (2) the pH value of the $0.0001m$ HCl solution at 350°C and 200 bars is 4.022 (calculated on the basis of the SLOP98 thermodynamic database). This is enough to determine pH from the measured E values for the whole series of solutions ($0.0003–0.1m$ HCl) (Table 1). Further, the HCl dissociation constant was fitted to the experimental pH values with the GIBBS program. In calculating the activity coefficients of all ions, the parameter $\mathring{a}$ equals 4.5 Å; the activity coefficient of nondissociated particles is accepted to be 1. As a result, $pK_{\text{dis}} = 2.16 \pm 0.03$ has been obtained.

The calculated value is consistent with the data reported by Tagirov et al. (1997) and Ho et al. (2001) but markedly differs (Fig. 4) from the results obtained by Lvov et al. (2000), Pokrovskii (1999), Grichuk (2000), and SLOP98 database. Judging by slopes of straight lines (Fig. 4), these results disagree with our potentiometric measurements.

Table 1. Results of E measurements in HCl solutions at 175–350°C and 200 bars

m HCl, mol/kg H_2O	Temperature, °C			
	175	250	300	350
	E, mV			
0.0003	507.3	526.6	594.4	680.1
0.00065	524.3	555.8	623.6	719.9
0.00095	–	574.8	–	735.4
0.00165	566	594.1	674.4	–
0.00285	–	622.9	–	781.5
0.0057	593.8	656.2	727.2	811
0.0195	652.5	710.9	772.2	865.5
0.032	–	726.4	–	883.9
0.107	722	770.1	855.8	917.2

SPECIATION OF ORE COMPONENTS IN SUBMARINE HYDROTHERMAL SYSTEMS

In many occurrences of recent submarine hydrothermal activity and associated sulfide ore, the temperature of outpouring fluids at the vent amounts to 320–370°C and the pressure, to 200–300 bars (Grichuk, 2000). Collected samples provide evidence for the pH value at 25°C. Typical black "smokers" are characterized by pH values ranging within 2.5–4.0. The fluid composition at natural temperature and pressure is estimated further from thermodynamic calculations. However, the question arises of how an uncertainty in determining the

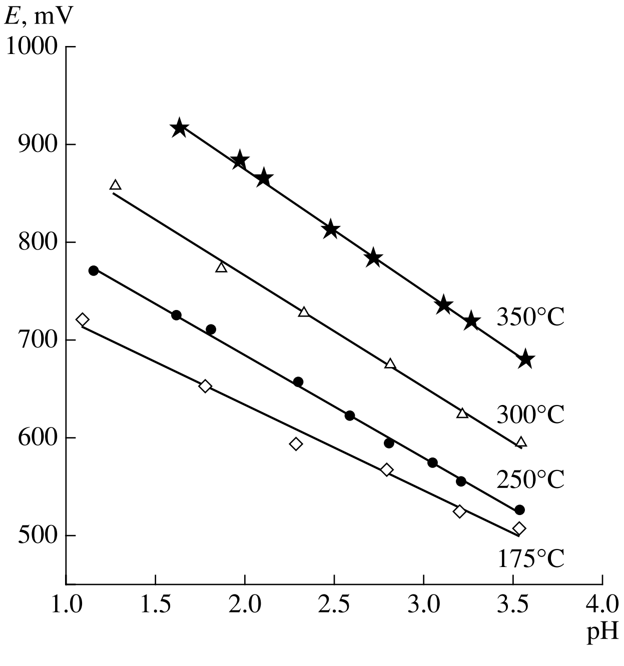

Fig. 3. Calibration plots at 175–300°C and the measurement results at 350°C and 200 bars.

Table 2. Comparison of experimental slopes of calibration straight lines in the *E*–pH coordinates with hypothetical slopes at 175–300°C and 200 bars

T, °C	Slope, mV/pH unit	
	experimental	theoretical
350		123.67
300	114.12	113.74
250	105.13	103.82
175	88.24	88.94

HCl dissociation constant may affect the results of such estimation.

To provide examples, we have recalculated the chemical analyses of two high-temperature solutions from the East Pacific Rise (HG spring) and Juan de Fuca Range (Monolith spring) described by Grichuk (2000). The recalculation was performed with the GIBBS program in two variants that include extreme values of the HCl dissociation constant based on (1) the data reported by Tagirov et al. (1997), which are consistent with the results of this work and (2) the data of Grichuk (2000). The thermodynamic properties of Au, Ag, and Cu aqueous species and of dissolved $H_2S^0(s)$ have been accepted after (Akinfiev and Zotov, 2004), and the thermodynamic properties of the remaining components of the aqueous solution and solid phases were taken from the SLOP98 database.

The calculation results are given in Table 3. They indicate that, though the calculated pH values vary up to ~0.5 pH unit, the speciation of ore components in both calculation variants virtually coincides. A slight difference in redistribution of chloride and hydrosulfide complexes is noted only for silver, copper, and gold.

According to the calculation, dissolved Fe, Mn, Pb, and Zn occur as various chloride complexes under the natural conditions of a hydrothermal vent. Silver and copper are represented 90–99% by chloride complexes ($AgCl_2^-$ and $CuCl_2^-$); as much as 10% neutral hydrosulfide complexes ($AgHS^0_{(s)}$ and $CuHS^0_{(s)}$) may be added, depending on H_2S content and acidity. In the case of Au-bearing hydrothermal solutions (Au was not established analytically), gold should be almost entirely represented by neutral hydrosulfide ($AuHS^0_{(s)}$) and, in a subordinate amount, by negative dihydrosulfide $Au(HS)_2^-$ complexes. The solutions were slightly oversaturated with pyrite and chalcopyrite.

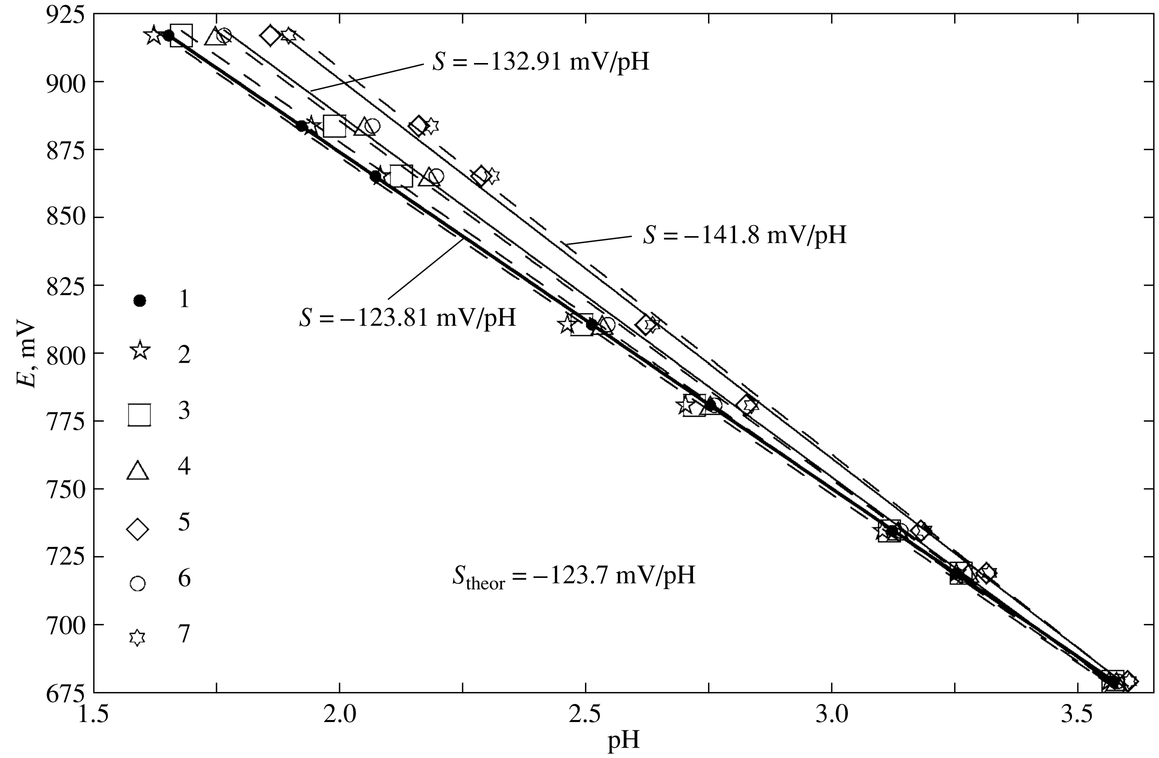

Fig. 4. The slopes of experimental straight lines in the *E*–pH coordinates versus the HCl dissociation constant at 350°C and 200 bars for HCl solutions (0.1–0.0003*m*). (1) This work (p*K* = 2.16); (2) Ho et al., 2001 (p*K* = 2.04); (3) Tagirov et al., 1999 (p*K* = 2.20); (4) SLOP98 (p*K* = 2.34); (5) Lvov et al., 2003 (p*K* = 2.38); (6) Pokrovskii, 1999 (p*K* = 2.42); (7) Grichuk, 2000 (p*K* = 2.73); lines are approximated with the least-squares method.

Table 3. Estimation of pH and speciation of ore components in high-temperature hydrothermal fluids of the East Pacific Rise and the submarine Juan de Fuca Ridge versus the chosen values of the HCl dissociation constant

Hydrothermal system		East Pacific Rise, 21° N, HG spring		Juan de Fuca Ridge, 45° N, Monolith spring	
Source of thermodynamic data for $HCl_{(aq)}$		Tagirov et al. (1997)	Grichuk (2000)	Tagirov et al. (1997)	Grichuk (2000)
component, parameter	complex, %				
T, °C		351		327	
P, bar		260		260	
pH (25°C, 1 bar)		3.3		2.8	
pH (*T*, *P*)		4.40	4.77	3.80	4.26
H_2S, mmol/kg		8.4		3.7	
	$H_2S^0_{(s)}$	99.9	99.9	99.9	99.9
	HS^-	0.1	0.1	0.1	0.1
Fe, mmol/kg		2.429		4.9	
	$FeCl^0_{2(s)}$	98	98	98	98
	$FeCl^+$	2	2	2	2
Mn, mmol/kg		0.878		1.94	
	$MnCl^+$	100	100	100	100
Pb, µmol/kg		0.359		1.09	
	$PbCl^0_{2(s)}$	53	53	37	37
	$PbCl_3^-$	39	39	43	43
	$PbCl_4^{2-}$	8	8	20	20
Zn, µmol/kg		104		580	
	$ZnCl^+$	50	50	43	43
	$ZnCl^0_{2(s)}$	48	48	53	53
	$ZnCl_3^-$	2	2	4	4
Cu, µmol/kg		44		7.8	
	$CuCl_2^-$	94	88	97	99
	$CuCl^0_{(s)}$	–	–	1.5	–
	$CuHS^0_{(s)}$	6	12	1.5	1
Ag, nmol/kg		37		88	
	$AgCl_2^-$	96	94	99	99
	$AgCl^0_{(s)}$	2	1	1	1
	$AgHS^0_{(s)}$	2	5	–	–
Au, nmol/kg		4*		10*	
	$Au(HS)_2^-$	3	7	–	1
	$AuHS^0_{(s)}$	96	93	84	93
	$AuCl_2^-$	1	–	15	6
	$AuCl^0_{(s)}$	–	–	1	–

Note: The composition of solutions is given after Grichuk (2000). The calculation was performed for two different values of the HCl dissociation constant reported by Tagirov et al. (1997) and Grichuk (2000).

* No gold was detected in these analyses. The concentrations are conditional.

CONCLUSIONS

(1) A technique has been developed for pH measurement at temperatures up to 350°C and pressures up to 350 bars in a flow-through cell of a nonisothermal cell consisting of a $ZrO_2(Y_2O_3)$ ceramic electrode and a Ag/AgCl (2 M KCl, 25°C) flow-through reference electrode.

(2) This technique was successfully employed for determining the HCl dissociation constant at 350°C and 200 bars, i.e., under conditions in which HCl dissociation has not been studied sufficiently reliably.

(3) As has been illustrated by the estimation of the chemical composition of submarine hydrothermal solutions, insignificant variations in the thermodynamic properties of HCl that change the pH value by 0.3–0.5 pH unit virtually do not affect the speciation of ore components in the fluids. A greater uncertainty may be related to possible alteration of the fluid composition in the course of sampling (loss of dissolved gases, precipitation of solid phases, etc.). In this regard, the on-site measurement of chemical parameters, pH value above all, becomes imperative, the more so as such measurements are technically feasible now.

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